EOARD-TR-77-04

February 28, 1977

FINAL SCIENTIFIC REPORT

6

ENERGY MIGRATION INVOLVING IRRADIATED SOLIDS

Period Covered

1.V.1976 – 31.X.1976

Professor Joseph Cunningham,
University College Cork,
Ireland.

DDC

MAY 24 1977

C

AD A039803

AD No.

DDC FILE COPY

correct
contract number 6 May 7?

is AF-AFOSR-2986-76
per Mrs. Bloce 11:15 *rol*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. Report Number EOARD-TR-77-04	2. Govt Accession No.	3. Recipient's Catalog Number
4. Title (and Subtitle) ENERGY MIGRATION INVOLVING IRRADIATED SOLIDS.		5. Type of Report & Period Covered Final rept. 1 May – 31 Oct 1976
		6. Performing Org. Report Number
7. Author(s) Joseph Cunningham		8. Contract or Grant Number AF – AFOSR-2686-76
9. Performing Organization Name and Address Department of Chemistry University College Cork, Ireland		10. Program Element, Project, Task Area & Work Unit Numbers 61102F 9767-99-54
11. Controlling Office Name and Address European Office of Aerospace Research and Development/LNC Box 14, FPO New York 09510		12. Report Date 28 Feb 1977
		13. Number of Pages 42
14. Monitoring Agency Name and Address European Office of Aerospace Research and Development/LNC Box 14 FPO New York 09510		15. 39 p.
16. & 17. Distribution Statement Approved for public release; distribution unlimited.		
18. Supplementary Notes		
19. Key Words ENERGY MIGRATION PASSIVATION NITROUS OXIDE IRRADIATED SOLIDS ELECTRON TRANSFER SITES METAL OXIDES		

20. Abstract

Results are presented which point to surface sites involving O^- ions and/or hydroxyls as important locations for transfer of energy via radiationless process between uv-illuminated metal oxides and probe molecules adsorbed on their surfaces. Attempted passivation of the surfaces by treatment with water vapor enhanced rather than decreased, the extent of interaction between irradiated solid and various probe molecules, including nitrous oxide or methyl halides as electron-accepting probe molecules or C_2D_5OD as an electron donating probe molecule.

FORM 1473

408 586

TECHNICAL SUMMARY

The research carried out under this short low-cost grant mainly represents an extension of a research effort previously funded under AFOSR-71-2148E. Since the Interim and Final Scientific Reports of that preceding grant provide a detailed account of the extensive publications and scientific communications arising from earlier phases of this research, such information is not repeated here, but the earlier reports should be referred to for an overall view of this research effort. In this extension of that research effort experiments have been designed and carried out to examine the exact nature of sites on the surface of irradiated solids which facilitate the transfer of radiation energy to gaseous 'probe' molecules present over the irradiated solids. In line with the agreed statement of work, these studies have included investigations of zinc oxide, magnesium oxide and titanium oxide as irradiated solid substrates; whilst nitrous oxide and alcohols have been used as gaseous probe molecules. This report includes a preprint of a paper describing results of such studies and entitled:
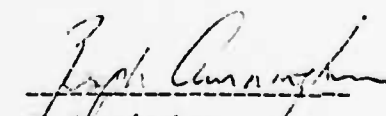
"Reactions Involving Electron Transfer at Semiconducting Surfaces, Part VII. Interactions of Nitrous Oxide and C_2-C_4 alcohols on ZnO and TiO_2 at Room Temperature".

That paper has been submitted for publication and it details evidence to support the conclusion that, for dehydroxylated ZnO or TiO_2 surfaces, the formation of O^--type surface intermediates and their subsequent reactions with adsorbed probe molecules (such as aliphatic alcohols) represent a sequence of radiationless processes which effectively convert energy absorbed from incident UV radiation into chemical changes in the adsorbed probe molecules. The preprint also demonstrates that attempted "passivation" of the ZnO and TiO_2 surfaces by treatment with water vapour at 623 K did not affect the reactivity of the dark or uv-illuminated TiO_2 surfaces but did markedly increase the activity of ZnO surfaces for dissociation of nitrous oxide both in the dark and

and additionally under UV-illumination. Although not reported
in the preprint, it has also been found that such attempted passiv-
ation of MgO surfaces increased their photocatalytic activity
for N_2O dissociation, but did so only for photons with $\lambda > 254$ nm.
These results upon attempted passivation of ZnO, TiO_2 and MgO
surfaces strongly suggest: (i) that surface locations involving a
"dangling" surface hydroxyl (which are not known to form on TiO_2 in
our conditions) can act as effective sites for transfer of electrons
from ZnO or MgO; (ii) that for semiconducting substrates such as
Zinc oxides with significant densities $(10^{14}-10^{18}$ cm^{-3}) of electrons
already in the conduction band at room temperature in the absence of
uv-illumination, these sites involving dangling hydroxyls allow
electron-transfer to probe molecules in the dark; (iii) for
insulating substrates such as MgO which lack conduction band electrons,
electron transfer becomes possible from sites involving dangling
hydroxyls wherever they interact with surface excitons.

The validity of these ideas has been further tested by experiments
with methyl halides CH_3Cl and CD_3I, which were selected because, like
N_2O, they were reported to be reactive towards electrons but not
towards the radical species OH or H. A total absence of photocatalysed
dissociation of the methyl halides was noted over uv-illuminated TiO_2
surfaces, which again appeared consistent with absence of hydroxyl-
containing surface sites for electron transfer on TiO_2. On dehydroxylated
MgO surfaces photocatalysed dissociation of the methyl halides occurred
to methane (80%) plus ethane (20%) but the same surface, after
rehydroxylation produced only methane product. The results were
consistent with the idea detailed above that presence of surface
hydroxyls facilitate reaction of surface excitons with the electron-
trapping probe molecules. An important role for surface sites
involving hydroxyls has thus been established in energy transfer
from irradiated ZnO and MgO to N_2O and methyl halide. probe molecules.

J. Cunningham
Principal Investigator

"Reactions Involving Electron Transfer at Semiconducting Surfaces[1]:
<u>VII</u>, Interactions of nitrous oxide and C_2 -C_4 alcohols on ZnO and TiO_2
at Room Temperature"

Joseph Cunningham and D.J. Morrissey

Department of Chemistry, University College, Cork. Ireland.

ABSTRACT

Trace amounts of dehydration product desorbed from Zno or TiO_2
surfaces upon exposure to t-butanol at room temperature whereas alkene
products from dehydration of ethanol or isopropanol were only detected
following thermally assisted desorption. Dehydration product was not
enhanced by nitrous oxide which did, however, increase extent of
alcohol dehydrogenation and yield additional nitrogen product from N_2O
dissociation. Extent of dehydrogenation and of additional nitrogen
formation correlated well with reported reactivity of alcohols towards
O^- fragments, which are here attributed to N_2O dissociation. Illumin-
ating the Alcohol/Metal Oxide interfaces with photons at 254 nm in a
dynamic system with on-line mass spectrometric analysis showed that,
with N_2O present, illumination further enhanced dehydrogenation and
nitrogen formation. Results are consistent with an important role for
coordinatively unsaturated oxygen ion sites in dehydrogenation and with
their conversion to surface O^- species by hole trapping. Dehydration
was largely unaffected by uv-illumination whilst presence of N_2O
influenced it in opposite sense to dehydrogenation. Sites active in
dehydration are tentatively identified as Lewis acid type metal ion
sites on the surfaces.

Earlier papers in this series considered electron-transfer from semiconducting ZnO or TiO_2 to adsorbed molecules, both in terms of *indirect* electron transfer based on collective-electron Band Theory models, and in terms of *direct* electron transfer from isolated electron-donating sites on the ZnO or TiO_2 surfaces[2,-5]. Metal-ion sites possessing lower-than-usual charge and higher-than-usual degree of coordinative unsaturation i.e. $M_{(cus)}^{(n-1)+}$, were identified as sites effective in direct electron-transfer to adsorbed N_2O or O_2. Examples were Ti^{3+} ions adjacent to oxygen vacancies on the surface[5] of TiO_2 and interstitial Zn_Δ^+ on the surface[2,3] of ZnO. It was recognised that if equilibration of electrons between such sites and the conduction band of these n-type semiconducting solids occurred rapidly via. $\underline{\underline{I}}$,

$$M_{(cus)}^{+n} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} M_{(cus)}^{+(n-1)} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} M_{(cus)}^{+(n-2)} \quad \ldots\ldots\ldots\underline{\underline{I}},$$
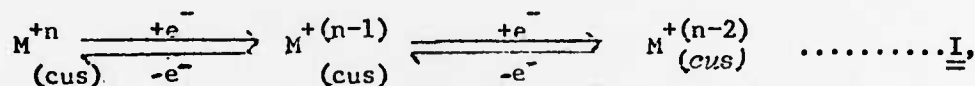
then the electron-donating power of these surface metal-ion sites should vary with position of the Fermi level. This prediction was confirmed[2,5] by careful measurement of the very small amounts of nitrogen product evolved from surfaces of various zinc oxides by dissociative-electron-attachment to nitrous oxide at room temperature according to $\underline{\underline{2}}$,

$$N_2O(g) \rightleftharpoons N_2O(ads) \xrightarrow{e^-} N_2O^-(ads) \longrightarrow N_2(g) + O^-\underline{(ads)} \cdot\underline{\underline{2}}$$
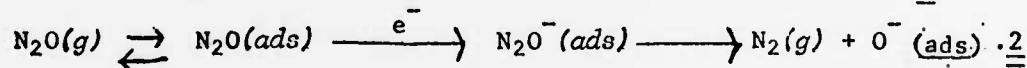
Other lines of evidence have also indicated electron exchange between bulk and surface locations of zinc oxides[6,7] but evidence has been lacking for corresponding exchange processes in TiO_2. Surfaces of TiO_2 powders have, however, been shown to donate[8,9,10] or accept[11,12] electrons from adsorbed organic molecules in certain conditions.

The present work extends to aliphatic alcohols our approach of utilising room-temperature reaction of surfaces with appropriate probe

molecules as a means of assessing number and nature of highly active surface sites. This extension of the approach was prompted by, and was designed to test, the following ideas advanced by previous workers in relation to surface activity for dehydrogenation and dehydration of aliphatic alcohols: *firstly*, the idea that primary and secondary alcohols are good reagents for electronic holes at surfaces of ZnO, either through direct interaction[13,14] or after hole capture by OH^-[15,16] The validity of these suggestions was of particular interest since, if correct, they would establish that alcohols could be used as hole-probes in similar manner to that already demonstrated for N_2O as an electron-probe in examining charge-localization at these semiconductor surfaces. Since concentrations of surface-localised holes were expected to be low for our n-type ZnO and TiO_2 samples in the dark at room temperature, present experimental tests of these suggestions include an examination of the interactions of alcohols with uv-illuminated samples having large concentrations of photogenerated holes. Such electronic holes in an array of lattice O^{2-} ions should possess some of the characteristics of O^- species[7]; *Secondly*, the idea that O^- exhibits selective reactivity towards primary and secondary, but not tertiary, alcohols, as previously postulated by Warman[17,18]. Warman further suggested that, when N_2O is used as the source of O^- species, secondary reactions 3a and 3b occur in the presence of primary or secondary alcohols and produce additional dissociation of N_2O.

$$O^- + ROH \longrightarrow (X+Y)^- \quad \dots\dots\dots\dots\dots\dots 3a$$

$$(X+Y)^- + a\ N_2O \longrightarrow a\ N_2 + (Products) \dots\dots\dots 3b$$
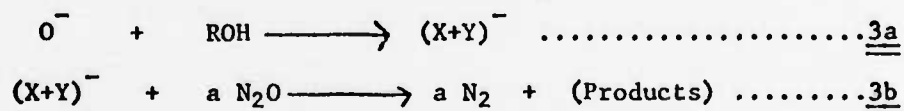
Insufficient information prevented identification of the ionic intermediates, $(X+Y)^-$, in the gas-phase reactions studied by Warman. However,

- 2 -

it was hoped that examination of analagous reactions on ZnO and TiO_2 surfaces in the present study would reveal surface processes similar to 3a and 3b and might clarify the nature of ionic intermediates and products on the metal oxide surfaces.

EXPERIMENTAL

Materials: Powdered, high-purity metal oxides were identical to the ZnO (SP500) and TiO_2 (Rutile MR-128) used in previous studies[2-5] and were obtained by courtesy of New Jersey Zinc Co. Thin polycrystalline layers on quartz substrates were prepared and activated at 623K as previously described. Alcohols were Analar reagent grade dried over freshly dehydrated molecular sieve and purified by trap-to-trap distillations, except for anhydrous C_2D_5OD or "$C_2D_5OD + 5\% D_2O$" which were used as supplied by Stohler Isotopes. High purity nitrous oxide, BOC Grade X, was used as obtained.

Procedures for non-illuminated samples: Observations on the gas phase above non-illuminated samples were made with the closed quartz reactor and associated greaseless high-vacuum system depicted in Fig.1a, wherein products were detected from room temperature interactions of alcohols and/or nitrous oxide with metal oxides previously activated for 16 hr. in vacuo at 623K. Products non-condensible (n.c.) at 77K were measured with Pirani or Ionization gauges and identified with a CEC type 21-620A mass spectrometer during periodic freezing-out of reactants into a trap at 77K. Since such measurements could only monitor growth of those products which desorbed from the catalyst surface at room temperature, a sequence of "desorption/pressure - measurement/mass analysis" was carried out with the system shown in Fig.1a while the catalyst, which had been exposed to

Alcohol and/or nitrous oxide at room temperature, was heated in vacuo by 50° increments to 623K. Electron spin resonance spectra were taken with a Decca X-1 spectrometer or a Varian model-, upon T_1O_2 samples to which alcohol was admitted as a vapour at room temperature.

Photoassisted Surface Reactions: Interfaces between Metal Oxide sample and Alcohol or (Alcohol+N_2O), which had completed the fast 'dark-reaction' characteristic of initial 0.5h contact times[5], were then illuminated by the low intensity output of a 15-watt low pressure Hg-arc lamp with emission mainly at 254 nm. Lamp configuration relative to the sample within an MgO-coated cavity was arranged to limit any possible surface heating effect to <5° temperature rise which, if induced thermally, did not significantly disturb the dark-equilibrated behaviour. Growth of any product which desorbed into the gas-phase at *room* temperature was followed and analysed over periods of illumination up to 6 hr. Photon flux at the sample position was determined by calibration with potassium ferrioxalate actinometer. Results obtained at illuminated interfaces are indicated by use of an asterisk e.g. N_2O/ZnO^* or C_2H_5OH/TiO_2^*. Photoassisted products were monitored *either* in the same system as for dark reaction (see Fig. Ia) *or* more directly in the dynamic flow system depicted in Fig. Ib. In this latter system, gases emerging from the reactor at pressures *ca.* $10^{-4} N m^{-2}$ entered into the ion source of a Micromass 6 mass analyser located 15 cm from the catalyst sample via. a high conductance path. Photoassisted changes in composition of the gas flow could thus be very rapidly detected and monitored.

RESULTS AND DISCUSSION

Section I: Formation and Desorption of Products in static reactors.

I.1. *Nitrogen product from N_2O/ZnO and $(N_2O + Alcohol)/ZnO$*
interfaces at room temperature:

Figure 2A(i) illustrates the rapid growth of gaseous product non-
condensible at 77K which occurred during the first hour of contact at
room temperature between freshly activated ZnO and nitrous oxide. Plot
(i) of Fig. 2B demonstrates that formation of noncondensible product over
the same ZnO surface in the dark at room temperature was slightly reduc-
ed when t-butanol was premixed with N_2O prior to contacting the freshly
activated surface. Plots (ii) of Fig. 2A and 2B demonstrate, however,
that the limiting yield of noncondensible product, $V(N_2)_{lim}$ as observed
at room-temperature contact times >60 min, was greatly enhanced when
either ethanol or isopropanol was premixed with N_2O in 1:1 mole ratio
and simultaneously contacted with the metal oxide. Mass spectrometric
analysis of the noncondensible product established that it was >98%
nitrogen and that no nitric oxide or oxygen was detectable. Empirical
kinetic analysis showed that the increase in nitrogen product, $V(N_2)_t$
detected after dark contact time t, obeyed the first-order type express-
ion,

$$\log \left(\frac{V(N_2)lim}{V(N_2)_{lim} - V(N_2)_t} \right) = k_d t \qquad (4),$$

for contact times 5 - 30 mins. Table I summarises the values of $V(N_2)_{lim}$
and k_d which gave the "best fit" of data to this expression. These data
point to two significant differences between the influence of tertiary as
distinct from primary or secondary alcohol at the N_2O/ZnO interface:

(a) Nett nitrogen product formation from nitrous oxide at contact times

TABLE I

Limiting yields of Nitrogen produced and desorbed over ZnO at room temperature

SYSTEM	$Po(React)$ Nm	$V(N_2)lim$ $mls/m^2 X10^{-5}$	$t_{\frac{1}{2}}(Min)$	θ_o-	$k_d(Min^{-1})$
N_2O/ZnO	45.0	4.16	8.1	0.011	$8.6X10^{-2}$
$N_2O+C_2H_5OH/ZnO$	45.0 (each)	7.73	7.7	0.019	$9.0X10^{-2}$
$N_2O+(CH_3)_2CHOH/ZnO$	45.0 (each)	7.76	8.4	0.019	$8.3X10^{-2}$
$N_2O+(CH_3)_3COH/ZnO$	45.0 (each)	3.53	4.1	0.009	$16.9X10^{-2}$

>1 hr., $V(N_2)_{lim}$, was approximately doubled by premixing ethanol or isopropanol with the nitrous oxide admitted to the freshly activated ZnO surface; whereas admixture of t-butanol slightly reduced $V(N_2)_{lim}$; (b) the apparently first-order rate constant, k_d, for dissociation of N_2O to N_2 at the 'dark' ZnO surfaces was not significantly affected by premixed ethanol or isopropanol, whereas t-butanol increased k_d, despite its overall inhibiting effect on $V(N_2)_{lim}$.

The effects noted for ethanol and isopropanol so strongly resemble those reported by Warman[17,18] (see Introduction) that a similar interprepation was suggested, viz. that initial dissociation of N_2O occurred via (2) on the metal oxide and that the resultant O^- *(ads)* species reacted rapidly with alcohol, producing surface intermediates, $(X+Y)^-$, which in turn rapidly dissociated other N_2O molecules via 3a and 3b. Such a mechanism, with process 2 containing the slow rate-determining step, would account for the overall rate constant k_d remaining unaffected by ethanol or isopropanol whilst the nitrogen yield $V(N_2)_{lim}$ doubled, since each type (2) event leads eventually via 3 to dissociation of at least two N_2O molecules. Our observation that t-butanol did not increase $V(N_2)_{lim}$ appeared consistent with Warman's conclusion that tertiary alcohols do not undergo type 3 reaction with O^-, and hence cannot lead to additional N_2O dissociation.

Data points to the right of an arrow on each plot in Fig. 2 show that illumination by UV light mainly at 254 nm caused additional photo-assisted dissociation to nitrogen product at ZnO interfaces which previously had attained their limiting value of $V(N_2)_{lim}$ in the dark. Two

- 6 -

contributions to this photoassisted dissociation can be distinguished on the traces in Fig. 2A: a slow linear growth of $V(N_2)^*$ with duration of illumination, which was the sole photoassisted process for N_2O/ZnO^*; and an initial rapid photoassisted growth $V(N_2)^*$, of nitrogen persisting only during the initial $\frac{1}{2}$ hr. of illumination at the $(N_2O + EtOH)/ZnO^*$ interface. For this latter interface the rate of photoassisted N_2 formation returned to that characteristic of N_2O/ZnO^* interfaces at illumination times $> \frac{1}{2}$ hr.

Data to the right of the arrows in Fig. 2B for mixtures of N_2O with isopropanol or t-butanol over the illuminated ZnO surface, also appear consistent with contributions by both an initial fast photoassisted process and a slower continuing process to growth of $V(N_2)^*$. Mass spectrometric analysis demonstrated that the apparent increase in n.c. product from illuminated t-butanol/ZnO*interface shown in Fig. 2B originated from photoassisted formation of methane and not N_2. This was the only illuminated interface found to yield appreciable desorption of methane product at room temperature and the significance of this observation is discussed in a later section.

Previous infra-red studies indicated a high degree of dehydroxylation for ZnO surfaces pretreated in vacuo at the 623-673K temperatures employed in the present study.[19] Isotopic composition of the methanes produced at such ZnO surfaces by interaction with CDI was likewise previously shown to be consistent with extensive dehydroxylation of ZnO activated at these temperatures.[4] Consequently the data in Fig. 2 for N_2 formation from N_2O/ZnO interfaces approximate to the situation for a dehydroxylated surface. It

TABLE 2

Limiting Yields of Nitrogen Produced and Desorbed over TiO_2 at Room Temperature

SYSTEM	P_o(React) Nm^{-2}	$V(N_2)_{lim}$ mls/m²×10⁻⁴	$t_{\frac{1}{2}}$(Min)	θ_o	k_d(min⁻¹)
N_2O/TiO_2	45.0	2.34	11.5	0.057	$6.02×10^{-2}$
$N_2O + C_2H_5OH/TiO_2$	45.0 (each)	6.90	5.1	0.176	$1.36×10^{-1}$
$N_2O + (CH_3)_2CHOH/TiO_2$	45.0 (each)	6.89	4.7	0.174	$1.49×10^{-1}$
$N_2O + (CH_3)_3COH/TiO_2$	45.0 (each)	2.01	5.7	0.049	$1.23×10^{-1}$

was of interest to rehydroxylate such ZnO surfaces and again observe
extent of nitrogen formation, in view of suggestions that surface
hydroxyls on metal oxides represent active surface sites. The ZnO
surfaces were rehydroxylated by baking in water vapour at 623 for 2
hrs. after which water was pumped away at 623 and the sample cooled
to room temperature. The growth of nitrogen product over this
rehydroxylated surface in the absence of illumination is represented
by curve(ii) of Fig.3A. Comparison with the initial 80 min. of curve(i),
which was obtained on the same ZnO layer prior to its rehydroxylation,
leaves no doubt that rehydroxylation yielded additional surface sites on ZnO
which were active for N_2O dissociation to N_2 at room temperature in the
static reactor. Curve(iii)of Fig.3A illustrates that UV illumination of
the interface between N_2O and rehydroxylated ZnO caused a further large
enhancement in the rate of N_2O dissociation. Thus it is clear that
rehydroxylated ZnO surfaces were much more active than dehydroxylated
ZnO for N_2O dissociation both in the dark and particularly under UV
illumination.

1.2. *Nitrogen product from N_2O/TiO_2 and $(N_2O+Alcohol)TiO_2$ interfaces at room temperature;*

Data to the left of the arrows in Figure 4 illustrates growth of
nitrogen product during the first hour of contact of freshly-activated
non-illuminated TiO_2 with N_2O or with (N_2O+Alcohol). Empirical kinetic
analysis again established that data for contact times 5-30 min. could
be adequately fitted to the first-order type expression $\underline{\underline{4}}$. Table 2
lists values so determined for $V(N_2)_{lim}$ and k_d over the TiO_2 surface.
Inspection of the $V(N_2)_{lim}$ values reveals that, at room temperature, t-
butanol failed to enhance nitrogen product formation at the dark $N_2O/$
TiO_2 interface, whereas admixture of ethanol or isopropanol greatly
enhanced $V(N_2)_{lim}$ relative to that with only N_2O present. Comparison

- 8 -

of data in Table 2 with Table 1 reveals that admixtures of ethanol or isopropanol with N_2O trebled the limiting yield of nitrogen product $V(N_2)_{lim}$ observed when contacted with TiO_2, in contrast to the doubling upon contact with ZnO. Since enhancement by a factor of 3 was just that noted by Warman[17,18] for reaction with gas-phase O^-, this observation suggested that O^- intermediates on TiO_2 surfaces reacted with these alcohols with stoichiometry similar to that reported for processes 3a and 3b in the gas phase. The smaller enhancement of (N_2) noted in Table I for corresponding ZnO interfaces could arise *either* from loss of some fraction of surface O^- radicals into the ZnO bulk by hole migration (which recent results of Lundsford support[7]) *or* by the blocking of some active sites on ZnO through rapid and irreversible chemisorption of alcohol (see below).

In contrast to ZnO interfaces, at which only t-butanol increased the apparently first-order rate constant k_d for N_2 formation from N_2O, all the alcohols caused k_d over $(N_2O+Alcohol)/TiO_2$ interfaces to increase to similar values approximately double those over N_2O/TiO_2. Unchanged values for $V(N_2)_{lim}$ with admixtures of t-butanol gave no evidence for occurrence of processes 3a or 3b with this alcohol. Consequently it appeared that only process 2 could contain a slow r.d.s. common to the three systems and that each alcohol enhanced this r.d.s. to comparable extent on TiO_2. Process 2 involves the sequence:- N_2O adsorption dissociation of N_2O within the surface; and finally, N_2 *desorption*. Data additional to those on rate of N_2 appearance in the gas phase would be necessary to determine which of these steps was enhanced by the alcohols to give rise to observed increases in k_d. Evidence on

- 9 -

this question is discussed in a later section.

Data to the right of an arrow in Fig. 4 were taken with photons of $\lambda=254$ nm incident onto the previously dark-equilibrated interfaces. The lack of any significant photoassisted dissociation to N_2 at the N_2O/TiO_2^* interface argued against significant photocatalysis of Process 2 at that interface. Consequently no photoassisted formation of additional $O_{(ads)}^-$ intermediates from N_2O was thought to occur at N_2O/TiO_2^* interfaces. Plots 4A(ii) and 4B(ii) demonstrate, however, that readily measurable rates of N_2 production were observed when ethanol or isopropanol were simultaneously present with N_2O at the illuminated TiO_2 surface. A working hypothesis capable of explaining these observations was that illumination of the TiO_2 surface directly produced surface $O_{(ads)}^-$ intermediates without the need to photodissociate N_2O, (e.g. by trapping photo-generated holes at pre-existing coordinatively unsaturated O^{2-} ions[20]).Reaction of adsorbed alcohol with such O^- entities via 3a to produce . secondary surface radicals capable of reacting with N_2O via. 3b, would account for the additional N_2 observed upon illumination despite the absence of O^- fragments from N_2O photodissociation. Absence of any photoassisted nitrogen product formation in the presence of t-butanol (see plot 4B (i) to the right of the arrow), is consistent with reported low reactivity of O^- towards this tertiary alcohol (recall that the photoassisted increase in noncondensible products from t-butanol/TiO_2 shown in Fig. 4 B plot (i) was due to formation of methane and not N_2)

Negative results of experiments aimed at establishing whether rehydroxylation of the TiO_2 surfaces enhanced N_2O dissociation to nitrogen are summarised in Fig. 3 B, which shows that growth of N_2 product followed

- 10 -

almost identical curves for dehydroxylated and 'rehydroxylated'
TiO_2 surface previously activated in vacuo at 623 for 16 hr.
was carried out in the same manner as for ZnO (viz. 2 hrs. in
water vapour at 623K) but figure 5.b. makes clear that this
treatment caused neither any increase in N_2 formation in the
dark nor any photoassisted N_2O dissociation. This result makes
it improbable that the enhanced dissociation of N_2O here observ-
ed in the presence of alcohol over the non-illuminated TiO_2
surface could have arisen from any rehydroxylation of the
surface by the alcohol. However, some workers report lack of
success in attempts to rehydroxylate TiO_2 surfaces[21] and the
conclusion that surface hydroxyls on TiO_2 are inactive for N_2O
dissociation must remain tentative until direct evidence becomes
available on the extent of surface rehydroxylation achieved with
H_2O or alcohol. Results of studies on the interaction of N_2O
and alcohols over ZnO or TiO_2 surfaces obtained on static
systems by other techniques are described in the following para-
graphs.

I. 3. *Products released by thermally-assisted desorption
from ZnO or TiO_2 interfaces previously exposed to
alcohol and/or N_2O.*

The t-butanol/ZnO interface was the only case in which
release of product into the gas phase accompanied room-tempera-
ture adsorption of alcohol onto ZnO or TiO_2 surfaces previously
activated in vacuo at $623^O K$ (cf.   Table 3). Our failure to
detect aldehyde or ketone products from the other alcohols in
the gas phase above the surfaces of these n-type semiconducting
solids did not appear fully consistent with previous claims
that a high Fermi level should promote dehydrogenation[22,23].

TABLE 3

Extent of Room-temperature Product formation at Alcohol Vapour/Metal Oxide
Interfaces - as deduced from thermal desorption in vacuo.

SYSTEM	Reaction Conditions	DESORBED PRODUCTS[a]			
Alcohol/Metal Oxide	at 390K	$(-H_2O)$	$(-H_2)$	(Diss)	$H_2(g)$
C_2H_5OH/ZnO[e]	dark	4.7	–	1.4[b]	17.0
"	+hν	5.0	–	1.9[b]	18.0
"	+N$_2$O	3.2	–	2.6[b]	14.0
"	hν+N$_2$O	4.4	–	2.7	15.0
C_2H_5OH/TiO_2[f]	dark	19.0	–	13.0[b]	0.6
"	+hν	19.0	–	4.1[b]	2.1
"	+N$_2$O	5.8	–	30.0[b]	0.2
"	hν+N$_2$O	2.6	–	12.0[b]	–
$(CH_3)_2CHOH/ZnO$[e]	dark	3.9	1.9	–	16.0
"	+hν	3.8	2.2	–	11.0
"	+N$_2$O	2.8	2.8	–	8.7
"	hν+N$_2$O	2.5	5.7	–	7.3
$(CH_3)_2CHOH/TiO_2$[f]	dark	69.1	–	6.8[c]	–
"	+hν	58.0	0.5	14.0	–
"	+N$_2$O	47.0	0.2	4.5[c]	–
"	hν+N$_2$O	44.0	1.6	9.9	–
$(CH_3)_3COH/ZnO$[e]					CH$_4$
"	dark	16.0	–	–	–
"	+hν	18.0	–	0.02[d]	–
"	+N$_2$O	16.0	–	0.01[d]	–
"	N$_2$O+h	17.0	–	0.12[d]	–
"	dark	0.06[g]			
"	+hν	0.09[g]		0.06[g]	0.07[g]
"	N$_2$O+hν	–		0.20[g]	0.09[g]
$(CH_3)_3COH/TiO_2$[f]	dark	81.0	–	–d	–
"	+hν	100	–	1.5	–
"	+N$_2$O	70.0	–	–	–
"	hν+N$_2$O	100	–	3.4	–
"	hν	4.2[g]	–	–	0.10[g]
"	N$_2$O+hν	1.7[g]	–	–	0.15[g]

a) Normalised to μl of product gas (STP) desorbing per m² of oxide surface.

b) Detected as butadiene + CO_2+methyl acetylene + propene.

c) Detected as acetaldehyde.

d) Detected as acetone.

e) Alkene and H_2 desorbed 300-460° but aldehyde on ketone 460-620K.

f) All product except acetone desorbed 300-510K but acetone desorbed 460-620K

g) Desorbed at room temperature.

Efforts were therefore made to detect the expected dehydrogenation products by thermal desorption after gas phase and any physisorbed alcohol had been pumped away at 300K away under continuous evacuation at $< 10^{-4}$ Nm^{-2}.

Data on these effects, which are summarised in Table 3, do not provide reliable absolute values for surface densities of sites active for alcohol dehydration or dehydrogenation at room temperature, because of possibilities for additional reaction during the thermal desorption procedure. They do, however, provide 'baseline' values for comparison with amounts of product thermally desorbed from the same interfaces in different conditions e.g., when exposed to uv-illumination or to nitrous oxide admixed with the alcohol.

Significant numbers of 'active sites' capable of alcohol dehydration were indicated by thermal desorption of corresponding alkene in readily measurable amount, (tabled under -H$_2$O in Table 3). This was true for both ZnO and TiO$_2$, but the specific activity of TiO$_2$ was greater in all cases. For the TiO$_2$ surface, extent-of-dehydration increased in the sequence, t-butanol>isopropanol>>ethanol, which is the same as that usually observed for alcohol dehydration by acid-type centres in homogeneous or heterogenous catalysis. Appearance of the olefine product at temperatures much below those previously reported indicates that some at least, of the dehydration sites were of unusually high activity.

As expected, no dehydrogenated product was obtained for
t-butanol but the ratio (dehydrogenation/dehydration) increased
for isopropanol and ethanol. Thermally assisted desorption
of the anticipated dehydrogenation products, (acetone or
acetaldehyde from isopropanol or ethanol respectively) occurr-
ed to lesser extent than release of dehydrated products or of
molecular hydrogen at temperatures <498K. The histograms in
Fig. 5 illustrate the higher desorption temperatures required
for release of acetone product than for propene or hydrogen
desorption from the isopropanol/ZnO interface. The acetone
histogram also represents (by the fully blackened sections)
the thermal desorption behaviour noted for the same surface
when acetone rather than alcohol was initially absorbed at
room temperature. At the higher temperatures required for
desorption of aldehydes or ketones, thermally-assisted rearrange-
ments occurred - as evidenced by partial conversion of pread-
sorbed acetone to isobutene or of preadsorbed acetaldehyde to 1,
3 butadiene. Extent of ethanol dissociation corresponding to
products related to adsorbed acetaldehyde is tabled under (Diss)
in Table 3. This latter observation contrasts with a report by
McArthur[26] that acetaldehyde desorbed readily from ZnO and the
difference suggests that ethanol selectively displaced acetal-
dehyde at the temperatures employed in McArthur's study.

Admixture of nitrous oxide with the ethanol admitted to
dark ZnO or TiO_2 caused a definite increase in products attribut-
able to acetaldehyde (which then suffered further degradation

- 13 -

upon thermal desorption). This observation, and a smaller

increase in acetone from isopropanol, appeared consistent

with the working hypothesis developed in Section I, according

to which nitrous oxide dissociated on the surfaces to yield O^-

fragments which enhanced dehydrogenation by then abstracting

α-hydrogen from primary or secondary alcohol. Data in Table 3

also show that dehydration products experienced a decrease

when N_2O was admixed with primary or secondary alcohols, in

contrast to the increases which N_2O brought about in dehydrogen-

ation.

A slight increase in extent of dehydration was observed

for t-butanol under illumination at either ZnO or TiO_2 surfaces

but nitrous oxide did not further enhance this photodehydration.

Comparison of the first and second data rows for other Alcohol/

Metal Oxide systems in Table 3 reveals that no significant

enhancement of dehydrated or dehydrogenated product above the

baseline values resulted from illumination of the interfaces

through a quartz wall with the output of a 15 watt low pressure

mercury arc lamp. Photons of λ 254 nm predominated in this

output and such photons had sufficient energy to create holes

and electrons in surface and sub-surface regions of the ZnO or

TiO_2 layers. Reports by previous workers, to the effect

that alcohols reacted with electronic holes at uv-illuminated

ZnO surfaces, had led us to expect additional oxidation of

alcohols at that illuminated interface relative to the baseline

values observed in the dark. Our failure to detect such addition-

- 14 -

al photoassisted dissociation of ethanol or isopropanol vapour
casts serious doubts on the idea that electronic holes pro-
mote alcohol oxidation. The last data line for the t-Butanol/
Metal Oxide system in Table 3 supports a similar negative con-
clusion, even when nitrous oxide and t-butanol were simultan-
eously present over these uv-illuminated interfaces. Particular
importance attaches to this latter observation because N_2O
represented a reducible, and t-butanol an oxidisable, reagent.
In terms of electronic theories[22], photogenerated holes and hole-
hole-electron pairs should promote their photoreduction and
photooxidation respectively. Consequently this negative result
argues against an important role of electronic factors at the
interfaces between illuminated ZnO or T_1O_2 and (t-Butanol +
nitrous oxide).

1.4. *ESR measurements:*

Further evidence of the small influence of adsorbed
alcohol upon electron localization/delocalization at the metal
oxide interface emerges from the ESR spectra shown in Fig. 6.
Spectrum (i) was measured at 77K on a sample of TiO_2 which had
been outgassed in vacuo at 623K and it corresponds well to
broad anisotropic adsorption band usually attributed to
paramagnetic Ti^{3+} centres at the TiO_2 surface. Spectrum (i)
was not significantly altered if the sample was warmed in vacuo
to 300K and again cooled to 77K but a new spectrum (ii) resulted
if such samples were exposed to the saturation vapour pressure of

ethanol or sec-2-butanol for 10 min. and re-evacuated at 300K before recooling to 77K. When such samples were subsequently heated to 623K under continuous evacuation and remeasured at 77K spectrum (i) was again obtained. The reversible nature of the change brought about by brief exposure to alcohol vapour at room temperature would be consistent with chemisorption of the alcohol. It must however be concluded from the small differences between spectra (i) and (ii), either in respect of integrated intensity or magnetic parameters, that surface paramagnetic Ti^{3+} centres were not markedly affected by the chemisorbed alcohol. The changes in shape of the resonance would be consistent with weak dipolar interaction between chemisorbed alcohol and Ti^{3+}, resulting in a slight increase in g_{11} of the latter.

The absence of any marked change in integrated intensity of the spectrum certainly would not be consistent with extensive charge transfer between alcohol and the vacuum-activated Ti_iO_2 surface. Thus if chemisorbed alcohol acted as a donor increase in Ti^{3+} centres would be expected. Conversely decrease in their number should have occurred if Ti^{3+} centres transferred electrons to chemisorbed alcohol.

SECTION II

Reactions of alcohols and/or (Alcohol+N_2O) mixtures at illuminated ZnO and TiO_2 surfaces under dynamic conditions.

Since results in Section 1 showed that aldehyde and ketone products from alcohol dehydrogenation reactions remained adsorbed on non-illuminated ZnO and TiO_2 surfaces in the *static*

- 16 -

reaction system and were only gradually desorbed on heating to $625^{O}K$ in vacuo, experiments were carried out in dynamic conditions to determine if products of photoassisted elimination reactions then remained adsorbed in similar manner, or if they were released to the gas phase at room temperature. Oxide samples were therefore prepared and pre-treated as described above and then exposed to low dynamic pressures of reactant gas(es) at ca $10^{-4}Nm^{-2}$, which were established over the samples as a balance between inlet leak-rate of reactants through a metal variable leak valve and their removal by a continuously operating ion-pump with pumping speed of 50 litres sec^{-1}. A micromass 6 mass analyser located 15 cm from the oxide surfaces along a high conductance path was employed for on-line gas analysis. Reactant alcohols, or (alcohol+N_2O) mixtures in approximately 1:1 mole ratio, were mass-analysed at various time intervals, prior to the commencement of illumination, until reproducible reactant spectra were obtained. Continuous illumination of the *GAS/SOLID* interface was then commenced and the gaseous phase mass-analysed at various times during an illumination period of approximately three hours. Inter-faces were illuminated through a quartz envelope by the unfiltered output of a 15-watt low pressure Hg lamp with output concentrated principally at 254 nm. and results are summarised in Figures 7A and 7B

II. 1. *Photoproducts from Isopropanol/Metal Oxide interfaces:*
On-line mass analysis provided no evidence for measurable enhancement of peaks at m/e values corresponding to propene, the dehydration product detected from ZnO interfaces by thermal desorption (cf. Section 1). Exposure of the illuminated ZnO surface

- 17 -

to alcohol was, however, several orders of magnitude less in these on-line analyses ($\underline{ca}$ 4×10^{-3} torr sec) than for typical exposures ($\underline{ca}$ 10^{3} torr sec) in the static reactor experiments.

The lower curve of Fig. 7A illustrates photo-assisted production of acetone dehydrogenation product upon illumination of an *isopropanol/ZnO**interface through quartz. Note the rapid initial increase in gas-phase acetone, reaching a maximum approximately 4 minutes after the commencement of uv illumination. This increase was followed by a slow decrease in dynamic pressure of acetone until, at times ~170 min. after the commencement of illumination, photoproduction of acetone had ceased. These results indicated that, as illumination proceeded in the presence of isopropanol, surface sites capable of photoassisted dehydrogenation were progressively removed. The results would be consistent with photogeneration of surface O^{-} sites and their reaction with isopropanol to yield dehydrogenated product plus inactive surface hydroxyls. Recent publications on reactivity of O^{-} show the requisite high rate constants for abstraction of α^{-}hydrogen[17, 25].

Data to the left of the arrow in the diagrams in Fig. 7 were obtained prior to the commencement of u.v. illumination and show that presence of N_2O and isopropanol in 1:1 mole ratio as the gas phase flowing over the 'dark' ZnO interface resulted in a larger pre-illumination level of acetone formation (Fig. 7A upper plot). Data to the right of the arrow in the upper plot show that the initial photoenhanced formation of acetone was larger and was sustained for longer times in the presence of N_2O.

- 18 -

These observations are consistent with some production of additional O^- species from N_2O on the dark or illuminated ZnO interface and reaction of these O^- species to yield dehydrogenated products via reactions of type 3a and 3b. Data on the upper plot of Fig. 7A at times >60 min. illumination indicate a small nett increase in acetone, corresponding to some small rate of photoassisted dehydrogenation in the photostationary state via 3a and 3b. Nitrogen corresponding to this process was detected in the static photoreactions (see Fig. 2A ii).

Data in Fig. 7B illustrate the photoassisted growth of both the dehydration product, propene, and the dehydrogenation product, acetone, above a uv-illuminated isopropanol/TiO_2* interface. Comparison of Figures 7A and 7B confirm the greater activity of the TiO_2 surface for these photoassisted elimination reactions involving isopropanol. Since ESR measurements on a previous study on the ZnO and TiO_2 samples used in this weak showed much greater surface concentration of metal-excess centres on TiO_2 than on ZnO, such Ti^{3+} centres are suggested as the active sites responsible for the greater dehydration on TiO_2.

II.2 *Comparison of photoassisted elimination reactions for primary, secondary and tertiary Butanols.*

summarises results of on-line mass analysis of photoproducts detected above uv-illuminated interfaces of TiO_2 with primary, secondary or tertiary butanol. Extent of observed photodehydration may be seen to lie qualitatively in the sequence expected on the basis of ease of alcohol dehydration, viz. tertiary >secondary>>primary. Since a quantitative measure of the extent of each photoassisted elimination reaction was desirable, values

for the total amount of gaseous photo-products which desorbed from the illuminated interfaces over the observed time-intervals were derived using equation (5),

$$\text{Amount desorbed} = \frac{1}{ART_0}\ V\Delta P\ (t) + s\int_0^t \Delta p\,dt \qquad (5)$$

In this equation, as developed in 1953 by Becker and Hartmann[26] A = surface area of adsorbent; T_0 = gas temperature; V = volume of reaction system; S = pumping speed and $\int_0^t \Delta p\ dt$ is the area under pressure-versus-time curves such as are shown in figures 7 and 8. Increases in peak height obtained experimentally for various mass numbers were converted to pressure changes Δp, and substituted into equation (5), thereby yielding values for the total number of molecules of each product desorbing in a given time interval, (usually 0-170 min. after the commencement by uv. illumination). These values are tabulated in Table 4 for the Alcohol/Metal Oxide systems studied. In relation to photo-dehydration, these data show that extent of reaction of tertiary butanol was an order of magnitude greater than for secondary alcohols at the same interface, whilst primary alcohols did not experience photodehydration to measurable extent. Extent of photodehydrogenation (see columns headed "$-H_2$" in Table 4) did not show such large variations with the nature of the alcohols,- which indicates that extent of this photoassisted elimination process depended more upon the number of active sites provided by the illuminated TiO_2 or ZnO surface than upon ease of alcohol dehydrogenation. Tertiary butanol represented an obvious exception to this behaviour since dehydrogenation via. an initial α-hydrogen abstraction was not possible. Our observations showed that acetone was the second major photoproduct from t-butanol/

TABLE 4

Extent of room temperature dehydration and dehydrogenation at alcohol vapour/ metal oxide illuminated interfaces under dynamic conditions.

Reactant	ZnO* $(-H_2O)$	$(-H_2)$	$(-CH_4)$	TiO$_2$* $(-H_2O)$	$(-H_2)$	$(-CH_4)$
C_2H_5OH	– .	2.5×10^{19}	–	–	1.1×10^{20}	–
$N_2O + C_2H_5OH$	–	6.9×10^{19}	–	–	2.3×10^{20}	–
$(CH_3)_2CHOH$	–	3.6×10^{19}	–	1.9×10^{19}	1.4×10^{20}	–
$N_2O + (CH_3)_2CHOH$	–	7.7×10^{19}	–	–	2.6×10^{20}	–
$(CH_3)_3COH$	1.1×10^{20}	–	7.4×10^{19}	1.8×10^{20}	–	1.8×10^{20}
$N_2O + (CH_3)_3COH$	8.4×10^{19}	–	9.9×10^{19}	6.1×10^{19}	–	$3.4 \cdot 10^{20}$
$(CH_3)_2CHCH_2OH$	–	2.9×10^{19}	–	–	7.8×10^{19}	–
$CH_3CH_2CH(OH)CH_3$	1.0×10^{19}	4.3×10^{19}	–	1.5×10^{19}	1.3×10^{20}	–

Metal Oxide* systems, in addition to isobutene. The overall
stoichiometry of acetone formation may be expressed as in (6).

$$(CH_3)_3 COH \xrightarrow[\text{MO}]{hv} (CH_3)_2 C = O + CH_4 \quad \ldots\ldots\underline{(6)}$$
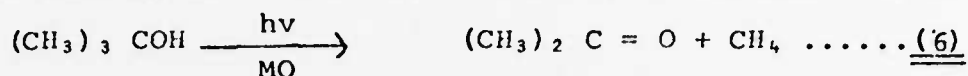
A reaction with this stoichiometry would be consistent
with the relatively large amounts of methane obtained on
illumination of the *t-butanol/metal oxide* interface in the
static reaction system (see Table 3). Such photoassisted
reaction may be described as "$(-CH_4)$", i.e. a photoelimination
of methane. Data listed under that heading in Table 4 indicate
the amount of acetone detected by on-line mass analysis. It
was originally felt that the formation of acetone at the
*t-butanol/ZnO** interface might be the result of secondary
reactions such as oxidation of isobutene photoproduct by
lattice oxygen. However, test experiments with mixture of
$(N_2O+isobutene)$ present over illuminated ZnO or TiO_2 surfaces
under either static or dynamic conditions did not result in
significant photooxidation of the isobutene. Dehydration
followed by oxidative cleavage of the double bond is therefore
discounted as a route to photoassisted elimination of the
methane observed from t-butanol. In effect the process has the
characteristics of a reverse Grignard reaction, which suggests
involvement of co-ordinatively unsaturated metal ion sites on
the catalyst surface. Further studies will be necessary before
the nature of the sites active for this process can be identi-
fied with confidence.

II.3 *Influence of water vapour in dynamic conditions.*

Since analysis with the on-line mass analyses offered a
more sensitive procedure (than static techniques) for examining

- 21 -

the influence of coadsorbed water upon photocatalytic activity, comparison was made of the extent of photoassisted formation of CD_3CDO from anhydrous C_2D_5OD and from C_2D_5OD containing 5% D_2O. Results are summarised in Fig. 8 for both ZnO and TiO_2 surfaces exposed to continuous illumination at 254nm. It is clear from these data that the presence of D_2O enhanced the extent of alcohol photo dehydrogenation. This is similar to reports by Stone et al[16] that rehydroxylation of a TiO_2 surface resulted in increased photodehydrogenation of isopropanol to acetone.

CONCLUSIONS

Results obtained in this study for the extent of N_2O dissociation at vacuum-activated ZnO or TiO_2 surfaces are fully consistent with the interpretation previously advanced that electron transfer to N_2O from unsaturated metal ion sites i.e., $M_{cus}^{+(z-1)} \xrightarrow{N_2O} (M^{+z} - O^-)_{cus} + N_2$, represents the main channel for nitrogen production at room temperature in the absence of uv-illumination. This model for surface reactivity is extended by the new data here presented on further dissociation of N_2O in the presence of primary or secondary alcohol, allied to the evidence for enhanced alcohol dehydrogenation when N_2O was present. Together, these observations are consistent with secondary reactions of the O^- ions formed from N_2O in this process . A necessary corollary to its efficient occurrence in the presence of N_2O is that other reactions requiring $M_{cus}^{+(z-1)}$ sites should be inhibited. The inhibition of alcohol .

- 22 -

dehydration here observed at surfaces also exposed to N_2O may thus be understood.

Results obtained here on photoassisted elimination reactions from alcohol vapours at ZnO or TiO_2 surfaces exposed to uv-illumination in static or dynamic conditions demonstrate the occurrence of other surface sites capable of interacting directly with alcohol when activated by illumination. Results with alcohols are consistent with identification of these sites as O^{2-}_{cus} and with their conversion to O^-_{cus} by hole-trapping during illumination. The enhancing effect of 5% D_2O upon photo-dehydrogenation of C_2D_5OD in dynamic conditions would be consistent with D_2O acting as an electron trap to complement such hole trapping. Present results do not, however, support the proposal that adsorbed alcohol act as efficient hole traps on ZnO or TiO_2, even when N_2O was simultaneously present as an electron trap.

Results here presented on changes in surface reactivity effected by treatments designed to rehydroxylate the vacuum-activated ZnO or TiO_2 surfaces point to important differences between the sites so produced on TiO_2 from those on ZnO, with only the latter effective for N_2O dissociation. Further study will be necessary to fully characterise such sites and determine if they are in agreement with recent suggestions[27] that O^{2-}_{cus} adjacent to surface OH^- can act as electron donor sites on ZnO and NO_2.

References

1. Work supported in part by funds from the U.S. Air Force Office of Scientific Research through EOAR under grants nos. 71-2148 and 76-2986.

2. Cunningham, J., Kelly, J.J., and Penny, A.L., *J. Phys. Chem.*, 74, (1970), 1992.

3. Cunningham, J., Kelly, J.J., and Penny, A.L., *J. Phys. Chem.*, 75, (1971), 617.

4. Cunningham, J., and Penny, A.L., *J. Phys. Chem.*, 76, (1972), 2353.

5. Cunningham, J., and Penny, A.L., *J. Phys. Chem.*, 78, (1974, 870.

6. Dewald, J.F. (a) *Bell System Tech. J.*, 39, (1960, 615 (b) *J. Phys. Chem. Solid*, 14, (1960), 155. (c) Cunningham, J. and Corkery, S., *J. Phys. Chem.*, 79, (1975), 933.

7. Lundsford, J.H., Taarit, Y.B. and Wong, N.B., *J. Chem. Phys.*, 60, (1974), 2148.

8. Che, M., Naccache, C. and Imelik, B., *J. Catalysis*, 24, (1972), 328.

9. Hosaka, H., Fujiwara, T. and Meguro, K., *Bull Chem. Soc. Japan*, 44, (1971), 2616.

10. Pimenov, Y.D., Kholmogorov, V.E., and Terenin, A.N., Doklady Akad Nauk S.S.S.R., 163, (1965), 935.

11. (a) Ueda, H. *Bull Chem. Soc. Japan*, 43, (1970), 319
    (b) Kiseler, A.V. and Urarov, A.V., *Surface Science*, 6, (1967), 399.

12. Davison, R.S. and Slater, R.M., *J.C.S. Farad. Trans.*, I, 72, (1976), 2416.

13. Morrison, S.R. and Freund, T., *Electrochem Acta.*, 13, (1968), 1343.

14. Gomes, W.P., Freund T. and Morrison, S.R., *J. Electrochem. Soc.*, 115, (1968), 818.

15. Bickeley, R.I. and Janaty, R.K.M., *Disc Farad Soc.*, 58, (1974), 194.

16. Bickeley, R.I. and Stone, F.S., *J. Catal*, 31, (1973), 389, 398.

17. Warman, J.M., *J. Phys. Chem.*, 72, (1968), 52.

18. Warman, J.M., *Nature*, 213, (1967), 381.

19. Atherton, K., Hockey, J.A. and Newbold Co., *Disc Farad. Soc.*, 52, (1971), 33.

20. Tench, A. and Nelson, R.L., *Trans. Faraday Soc.*, 63, (1967), 2254.

21. Primet, M., Pichat, P. and Mathieu, M.C., *J. Phys. Chem.*, 75, (1971), 1216.

22. Wolkenstein, T.L., *Electron Theory of Catalysis on Semiconductors* (Pergamon Press 1963).

23. Hauffe, K., *Adv. Catal*, 7, (1955), 213.

24. McArthur, D., Bliss, H. and Butt, J., *J. Catal*, 28, (1973), 183.

25. Zehani, D. and Rabani, J., *J. Phys. Chem.*, 75, (1971), 1738.

26. Becker, J.A. and Hartmann, C.D., *J. Phys. Chem.*, 57, (1953), 157.

27. Cordischi, D. and Indovina, V., *J.C.S. Farad. Trans.*, I., 72, (1976), 2341.

Captions to Figures

Figure 1   Vacuum systems for study of gaseous products evolved from interfaces of ZnO and TiO_2 with N_2O and/or aliphatic alcohols:

1(a) Static reactor with pumping line, P; gas handling line, L; pirani gauge, G; variable leak valve, V; metal valves, M; cold fingers, C; and metal oxide sample, M.O.

1(b) Dynamic reactor with inlet leak valve, I; metal oxide layer, M.O.; stainless steel tubing, E; glass walled photo-reactor, C; micromass 6 mass analyser, M.A.; pressure gauge, B; and ion pump.

Figure 2   Evolution of N_2 product from ZnO surfaces at 293K (position of arrow denotes commencement of illumination):

2A (i) N_2O/ZnO with $P_{N_2O} = 45$ Nm^{-2}.
   (ii) $N_2O + C_2H_5OH$/ZnO with $P_{N_2O} = 45$ Nm^{-2} $PC_2H_5OH = 45Nm^{-2}$.

2B (i) $N_2O + (CH_3)_3COH$/ZnO with $P_{N_2O} = 45$ Nm^{-2} $P(CH_3)_3COH = 45Nm^{-2}$.
   (ii) $N_2O + (CH_3)_2CHOH$/ZnO with $P_{N_2O} = 45$ Nm^{-2} $(CH_3)_2CHOH = 45$ Nm^{-2}.

Figure 3   Effects of surface rehydroxylation upon N_2O dissociation on ZnO or TiO_2 at 293K:

3A (i) N_2 evolution on ZnO surface pretreated in vacuo at 623K for 16 hours (arrow denotes start of illumination).
   (ii) As for (i) except surface rehydroxylated by treatment in 50 Nm^{-2} H_2O at 623K for 2 hours.
   (iii) As for (ii) except u.v. illumination commenced at time indicated by the arrow.

3B (i) N_2 from TiO_2 surface pretreated in vacuo at 623K for 16 hours
   (ii) As for (i) except surface rehydroxylated at 623K in 0.5 torr H_2O.

Figure 4   Evolution of N_2 product from TiO_2 surfaces at
            293K:

            4A (i) N_2O/TiO_2;
                (ii) $N_2O + C_2H_5OH/TiO_2$;

            4B (i) $N_2O + (CH_3)_3COH/TiO_2$;
                (ii) $N_2O + (CH_3)_2CHOH/TiO_2$.

Figure 5   Histograms for thermal desorption of various
            products from $(CH_3)_2CHOH/ZnO$ interfaces on
            heating to 623K:

               (i) H_2 evolution;(ii) propene;
             (iii) Acetone (darkened sections represents
                    thermal desorption of $(CH_3)_2CO$ from a
                    $(CH_3)_2CO/ZnO$ interface.

Figure 6   E.S.R. spectra of TiO_2 at 77K:

               (i) After activation for 16 hours at 77K.
              (ii) After exposure for 10 min. to C_2H_5OH at
                    293K followed by evacuation.

Figure 7   Time profiles for appearance of various products
            in the gas-phase, as detected with Micromass 6
            mass analyser with isopropanol flowing over the
            metal-oxide catalyst at $2 \times 10^{-4} Nm^{-2}$. Arrows
            denote the start of continuous illumination with
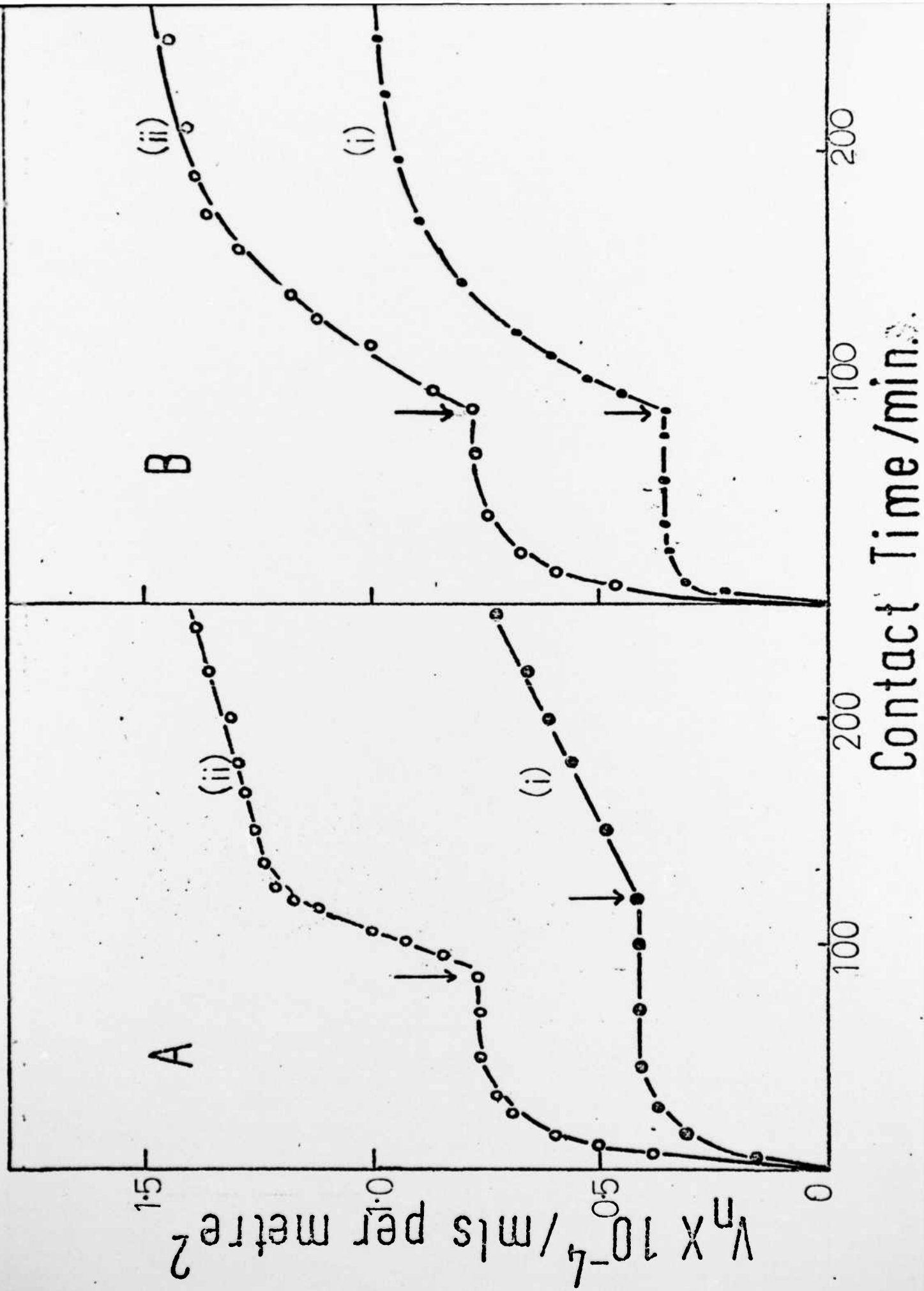   photons at 254 n.m.

            7A (i) Acetone from isopropanol/ZnO*.
                (ii) Acetone from N_2O + isopropanol/ZnO*.

            7B (i) Acetone from isopropanol/TiO_2*
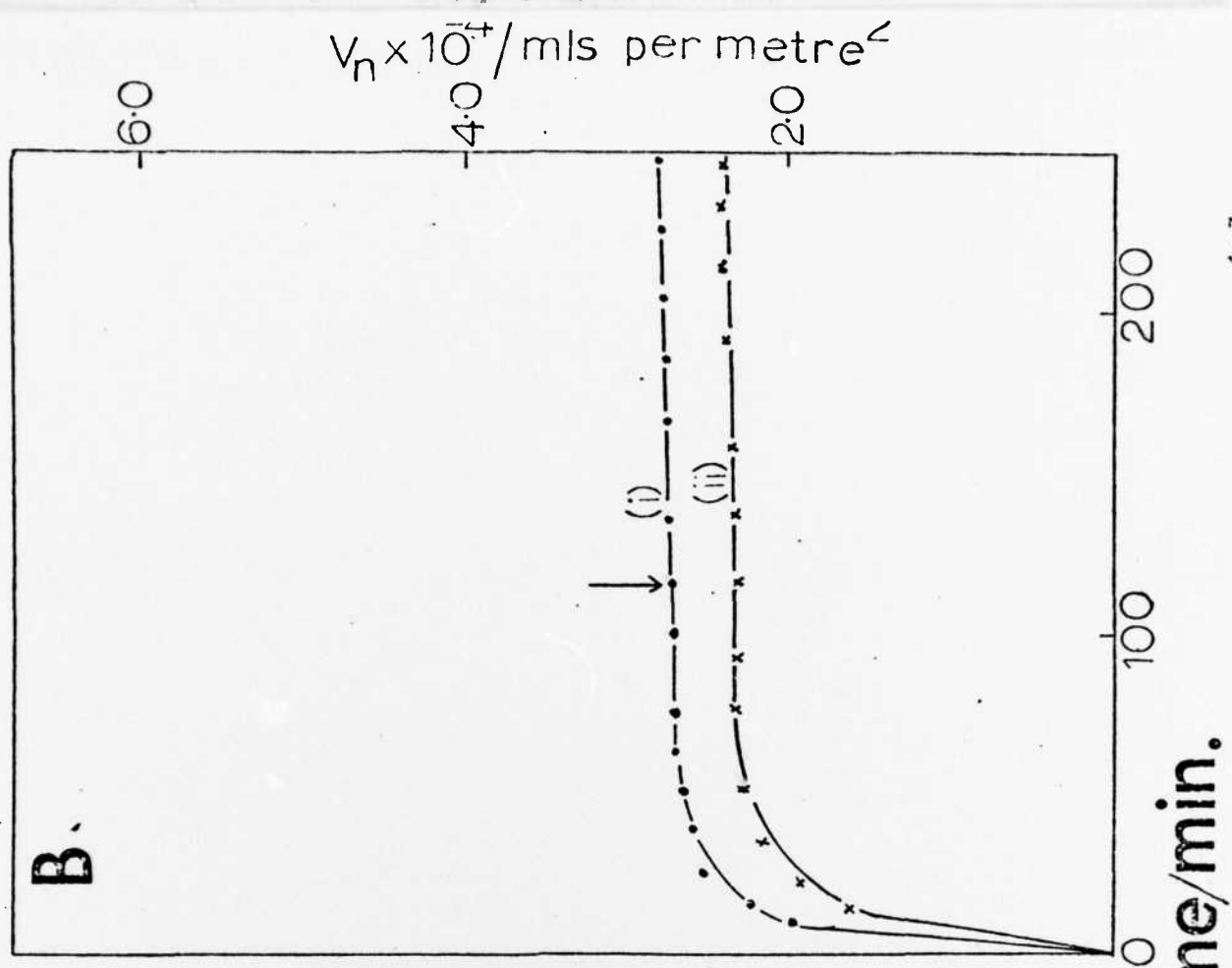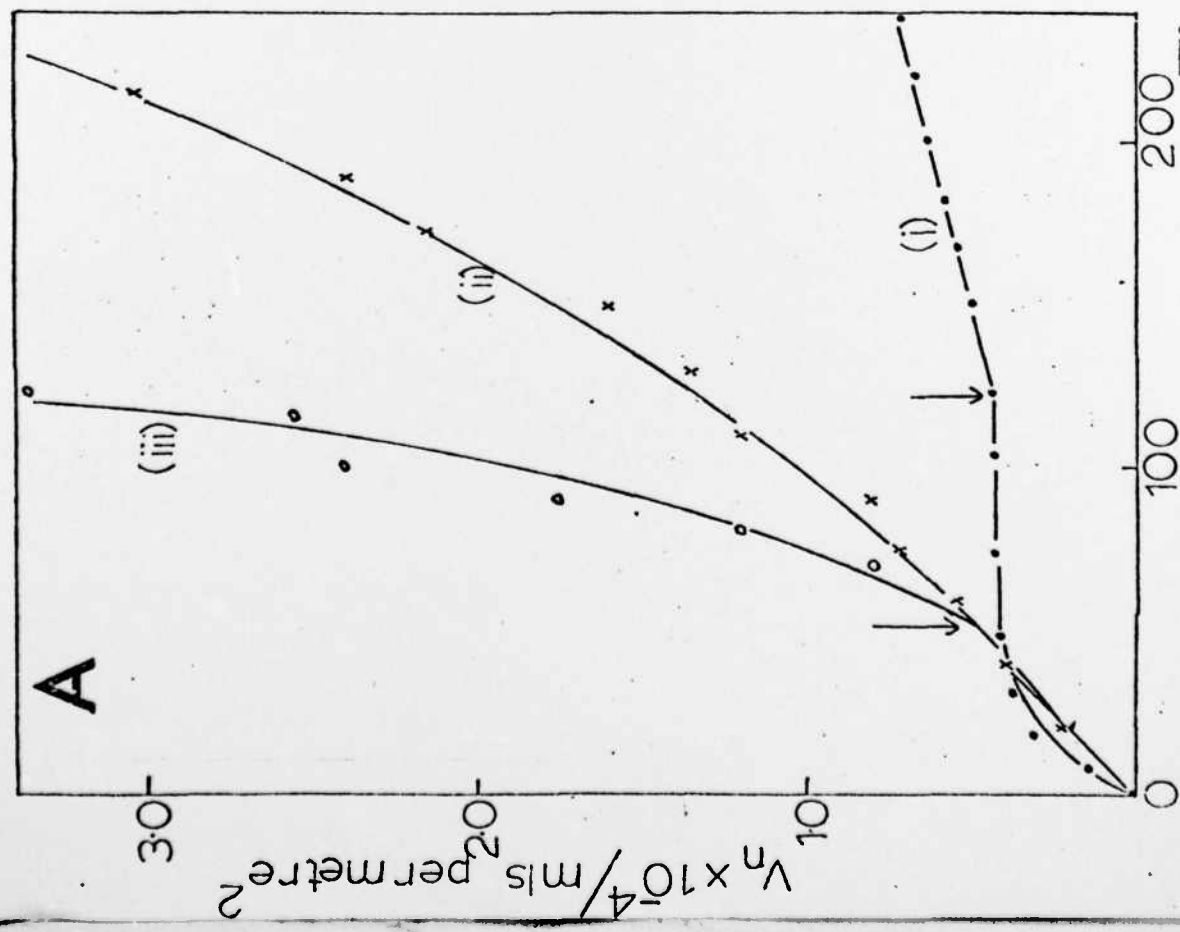

Figure 8   Influence of a 5% water content upon photodehydro-
            genation of ethanol over ZnO and TiO_2 surfaces
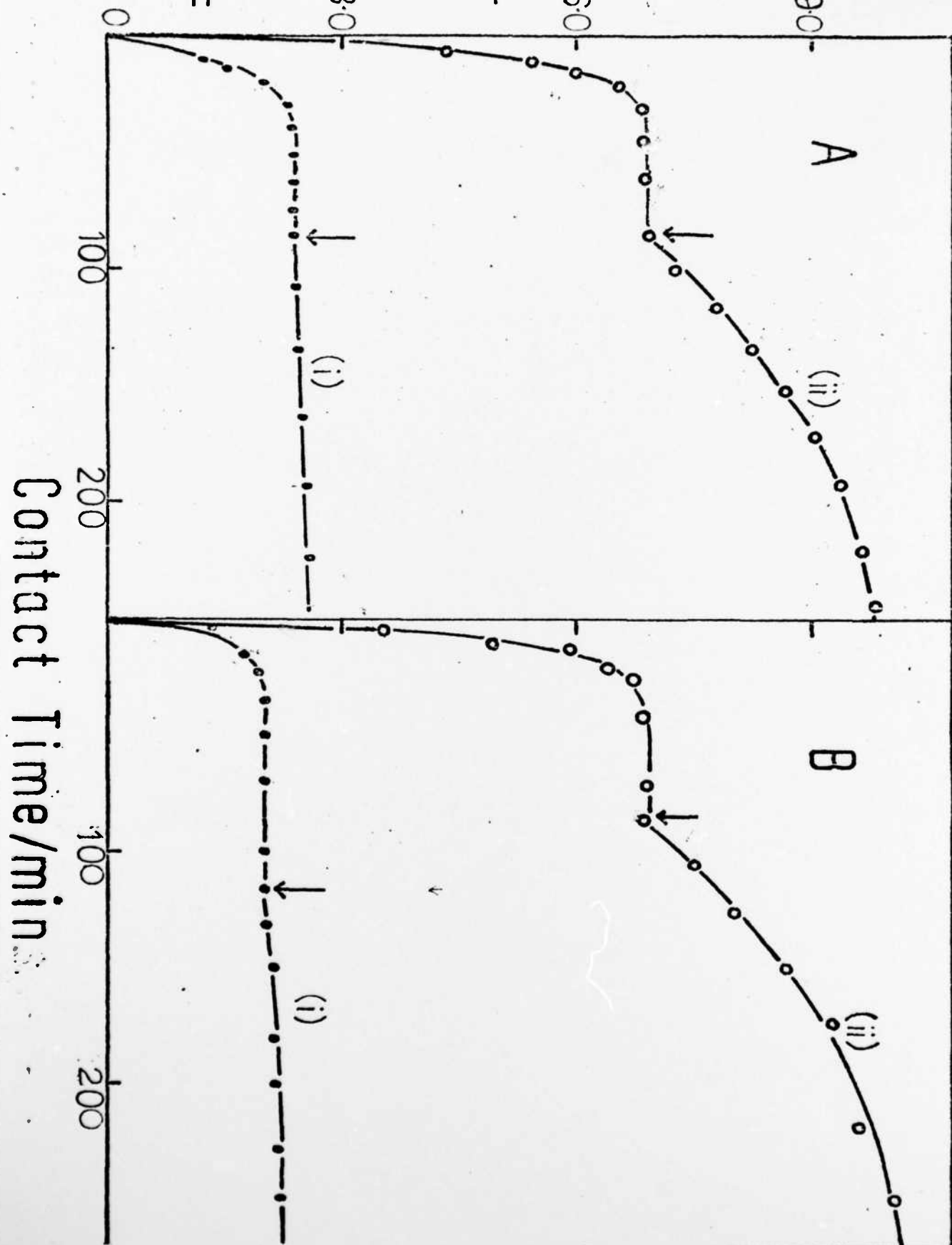   illuminated by 254 n.m. photons in a dynamic
            quartz photoreactor.

            8A (i) CD_3CDO from C_2D_5OD/ZnO*
                (ii) CD_3CDO from $C_2D_5OD + 5\%D_2O/ZnO$*.

            8B (i) CD_3CDO from C_2D_5OD/TiO_2*
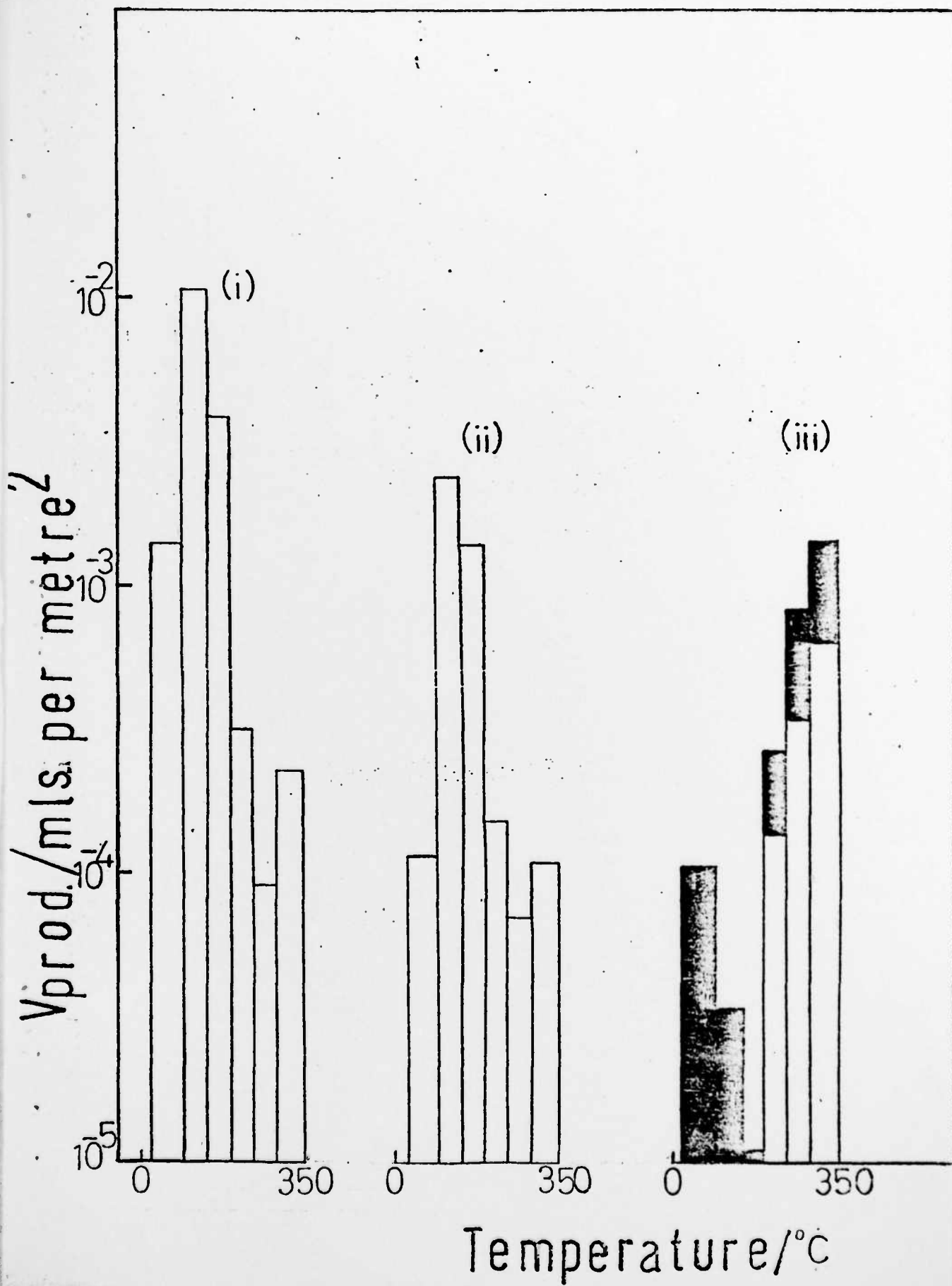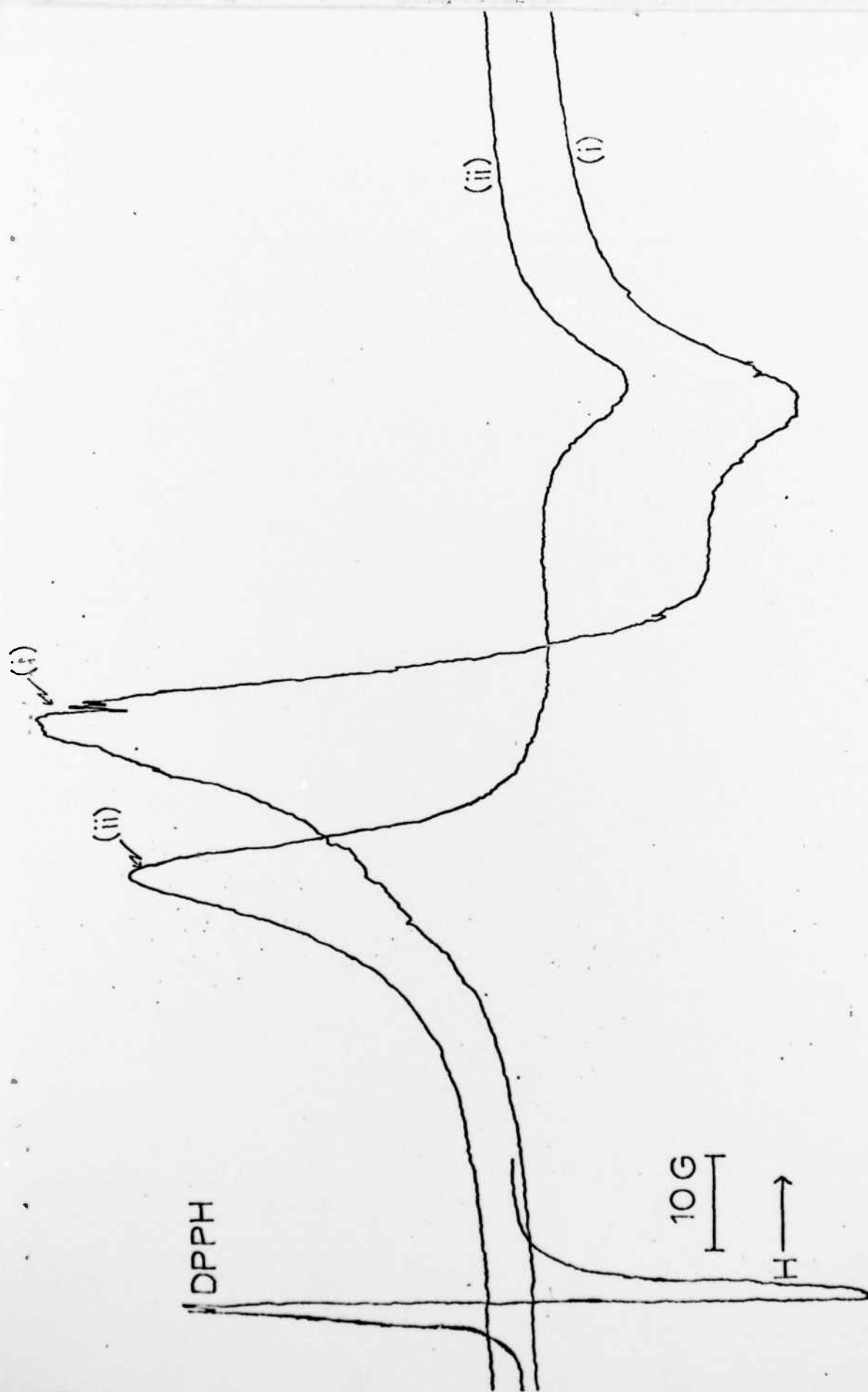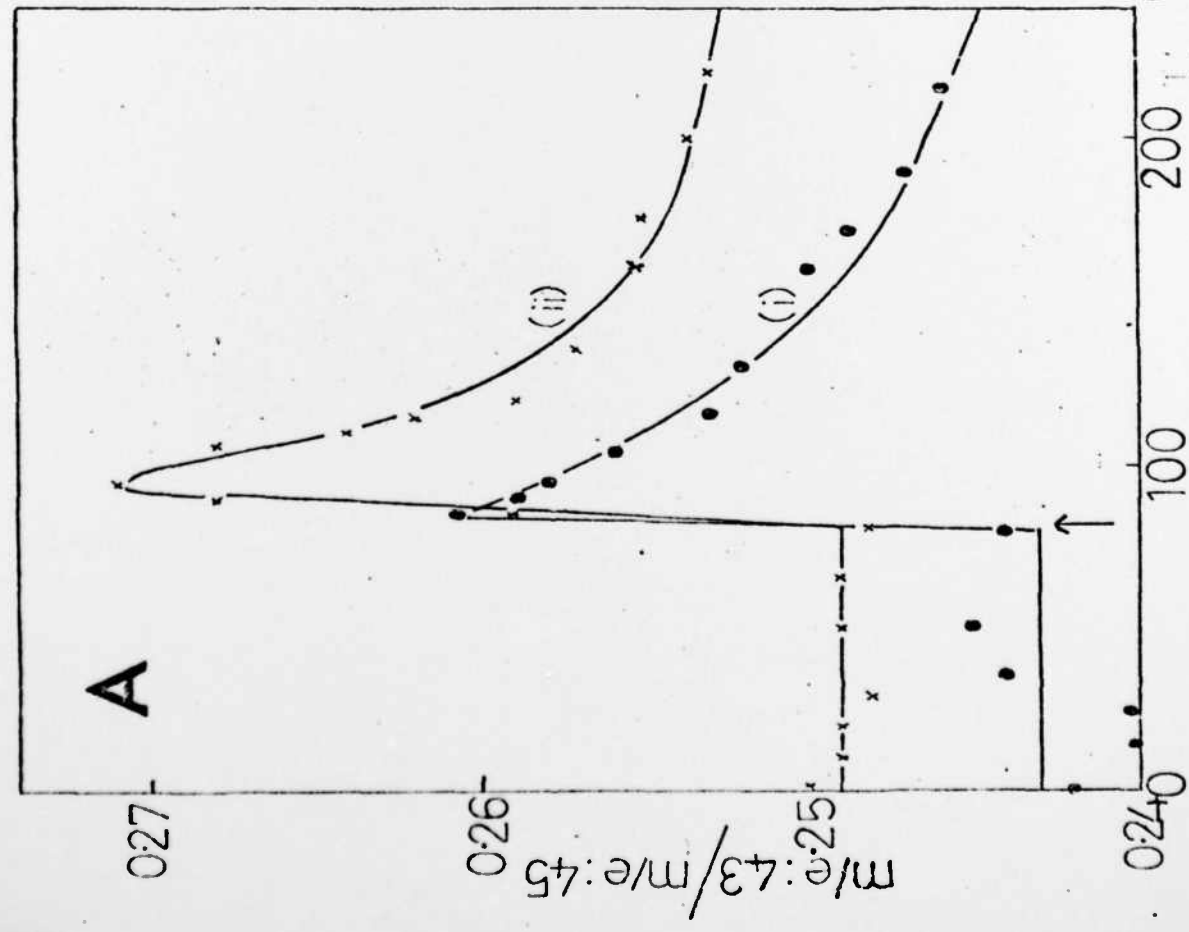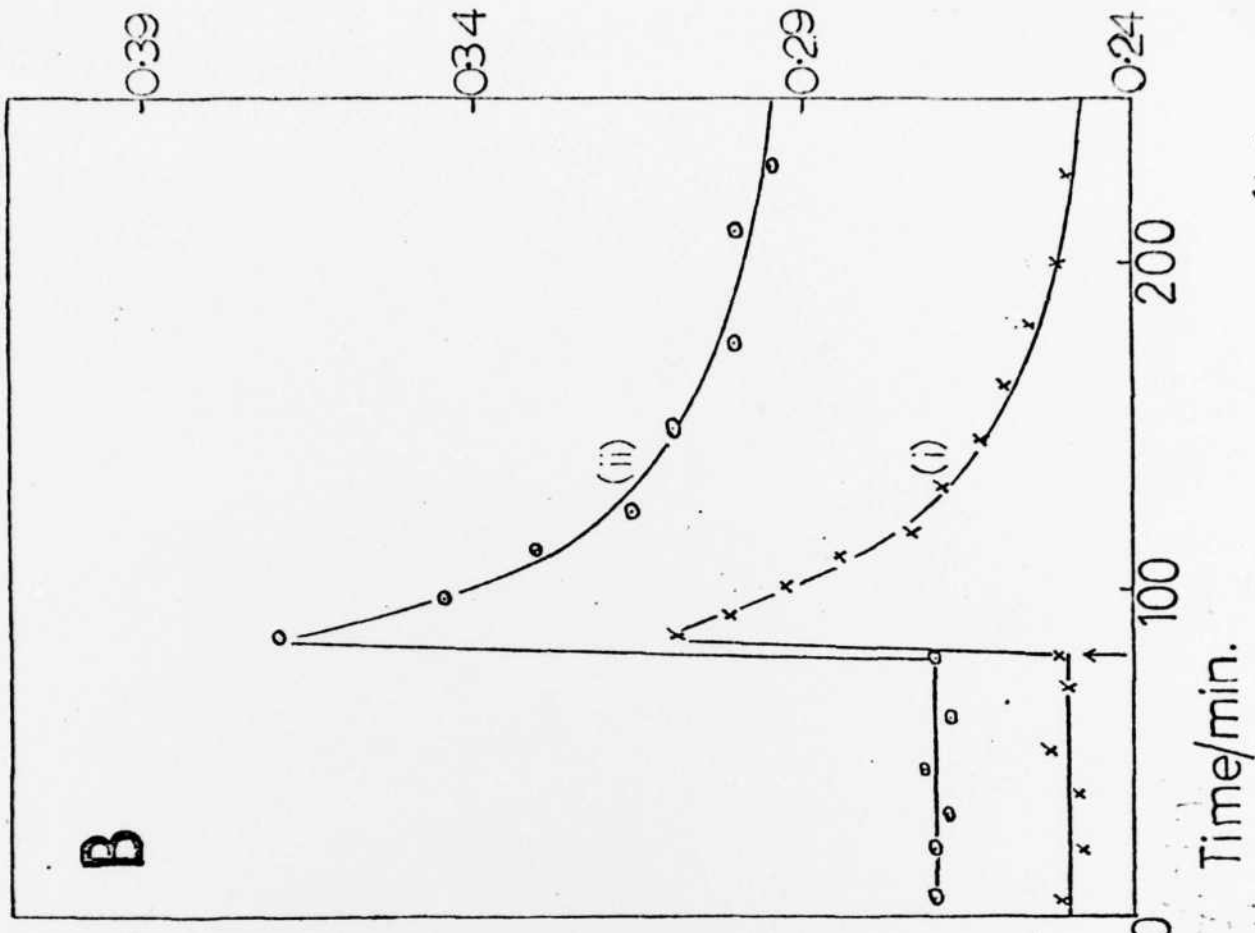   (ii) CD_3CDO from $C_2D_5OD + 5\%D_2O/TiO_2$*.

Fig.

B

I.P.

B

E

M.A.

C

M.O.

I

A

L

M

M

G

V

P

M

C

C

M.O.

C

Contact Time/mins.

$V_n \times 10^{-4}$/mls per metre^2

B.

Time/min.

$A_{4}3$

(i)

(ii)

A

(ii)

(iii)

(i)

$V_n \times 10^{-4}$/mls per metre^2

Figure: Plot of $V_n \times 10^{-4}$ / mls per metre^2 against Contact Time / min, showing panels A and B each with curves (i) and (ii).

DPPH

10 G

(i)

(ii)

(iii)

(iv)

H

Fig. 7

ATE
ME